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Equilibrium Studies on Interaction of Organotin (IV) Moieties with N-O Donor Ligands

Pratibha Paliwal (Bhatele)[1], Seema Yadav (Kumari)[2]

[1]Department of Science, Kamla Nehru College for Women, Phagwara, Punjab, India

[2]School of Studies in Chemistry, Jiwaji University, Gwalior, M.P, India

Abstract: ***Equilibrium studies of dioctyltin [DOT] (IV) and dimethyltin [DMT] (IV) Moieties with nitrogen and oxygen donor ligands i.e. glycine and alanine are investigated potentiometrically. Experiments are carried out in 10% alcohol medium at three different temperatures(20±1ºC, 30±1ºC and 40±1ºC) and at three ionic strengths(μ = 0.05M, 0.10M and 0.15M). The experimental data are subjected to computational analysis and thermodynamic parameters(ΔG° , ΔH° and ΔS°) for non protonated, monohydroxo and dihydroxo species have been calculated. The concentration distribution of the various complex species in solution has been evaluated as a function of pH and is presented in the form of speciation curves with the help of SCOGS computer program.***

Keywords: Pontentiometry, Organotin (IV), SCOGS, Thermodynamic parameters, Speciation Curves.

1. Introduction

Organotin compounds have emerged as potential future pharmaceuticals as antitumour agents in place of platinum antitumour drugs [1]-[4]. Thus, in order to get a better insight in how the organotin species behave inside the biological systems, it is necessary to explore their coordination chemical behaviour towards biomolecules that occur in the biological medium. Further, organotin (IV) compounds are widely distributed in environment owing to their intensive production for several industrial applications, e.g. as fungicides and acaricides in agriculture, as wood and stone preservatives, as stabilizers and catalysts in PVC and in foam production [5]-[8], and as antifouling additives in paints for ships [9]. In natural waters they can originate also from bio-alkylation processes [10].

In view of this, the studies based on interaction of organotin (IV) moieties with wide range of ligands becomes highly significant. Considerable efforts have been made to understand the binding mode of organotin compounds with biologically relevant ligands such as amino acids [11]-[14] and dipeptides [15], [16] which constitute a very important class of biomolecules.

Shoukry and his group of researchers published papers based on equilibrium studies of diorganotin (IV) moieties with amino acids and some selected ligands of biological importance [17]-[20].

It has been observed that most of the work is done in solid state and solution equilibrium studies have been less focused, which could provide essential information on the biospeciation of organotin moiety and thus on its bioavailability. The present communication describes the results of equilibrium studies on organotin (IV) moieties with nitrogen and oxygen donor ligands.

2. Experimental Details

2.1 Materials and reagents

All the chemicals used were of analytical grade and the solutions of ligands were prepared in doubly distilled CO_2 free water. DMT (IV) and DOT (IV) metal were prepared by dissolving their accurate weighed amounts in ethanol.

2.2 Equipments and Measuring Techniques

An Elico digital pH-meter model LI-127 with ATC probe and combined electrode type (CL-51B-Glass body; range 0-14 pH unit; 0-100°c automatic/manual) with accuracy ±0.01 was used for pH measurement. The pH meter was calibrated with aqueous buffers (pH 4.0 and 9.20) before and after titration.

Following sets of titration mixture were prepared with the ratio of 10% alcohol and 90% water by keeping total volume 50mL and titrated against 0.10M NaOH solution, ionic strengths (μ=0.05, 0.10, 0.15M) is maintained by adding different concentration of $NaNO_3$ solution to each titration mixture at temperature 20±1°C , 30±1°C and 40±1°C.
The complex of each titration mixtures is as follows:-

1. Mixture 1 :- HNO_3 (2.0×10^{-3}M) (Acid titration)
2. Mixture 2 :- HNO_3 (2.0×10^{-3}M) + ligand (1.0×10^{-3}M) (Ligand titration)
3. Mixture 3:- HNO_3 (2.0×10^{-3}M) + ligand (1.0×10^{-3}M) + Metal (1.0×10^{-3}M)
   (Metal : Ligand (1:1) titration)

3. Results and Discussion

3.1 Titration Curves

As a result of titration of set of three mixtures (1, 2 and 3) three titration curves were obtained for each system. These curves are presented in figures 1 and 2 as a plot of pH vs *'a'* where *a* = moles of alkali per mole of metal/ligand.

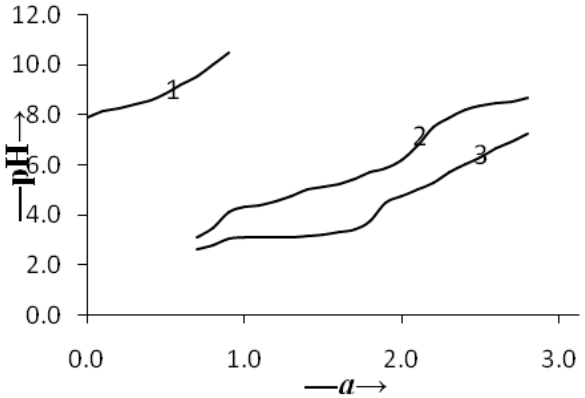

Figure 1: pH vs. '*a*' Curves for M(IV)-Glycine(1:1) System at 30±1°C[μ=0.10M($NaNO_3$)]

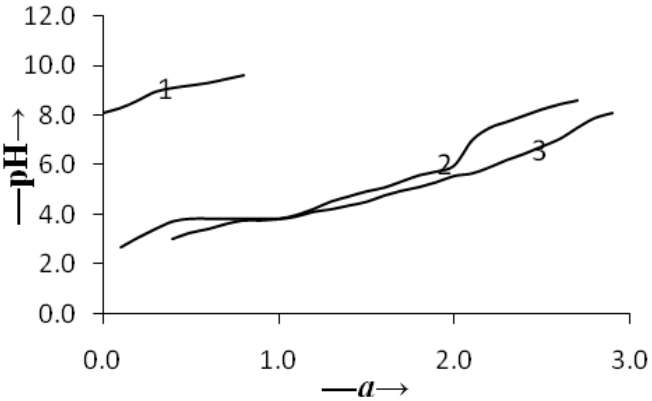

Figure 2: pH vs. '*a*' Curves for M(IV)-Alanine(1:1) System at 30±1°C[μ=0.10M($NaNO_3$)]

Curve 1- Ligand titration curve
Curve 2- DMT (IV)─ligand titration curve
Curve 3- DOT (IV)─ligand titration curve

Figures 1and 2 depict the interaction of DMT(IV)/DOT(IV) with glycine and alanine respectively. The observations lead to the conclusion that the proton dissociate in higher pH range (pH≈8.0) thereby indicating strong basic nature of ligands. The values of dissociation constants obtained agree well with the literature values [21].

Curves 2 and 3 in figures 1 and 2 depicting the titration of DMT (IV)─ligand / DOT (IV)─ligand respectively, show the right hand shift from the ligand titration curve 1, thereby suggesting the formation of metal─ligand complex in the pH ranging from 2.5 - 3.8. Further a weak inflection at a = 2 is observed in these systems, can be attributed to the formation of ML species by the deprotonation of MLH complex. This is followed by sharp inflections observed at a = 2 (pH ≈ 5.0) and a = 3 (pH ≈ 7.0) indicating the formation of monohydroxy ML(OH) and dihydroxy $ML(OH)_2$ species respectively.

These equilibria can be represented as follows:

$$M + L \underset{}{\overset{0 \le a \le 1}{\rightleftharpoons}} ML \qquad \text{----1.0}$$

$$ML + OH \underset{}{\overset{2 \le a \le 3}{\rightleftharpoons}} ML(OH) \qquad \text{----1.1}$$

$$ML(OH) + OH \underset{}{\overset{3 \le a \le 4}{\rightleftharpoons}} ML(OH)_2 \qquad \text{----1.2}$$

(Charges have been omitted for the sake of simplicity).

Algebraic method of Martell and Chaberek as modified by Dey et al. has been applied to calculate the values of equilibrium constants [22]-[25].

The values of protonation constants for various ligands and the formation constants of metal-ligand complexes are tabulated in tables 1-3. These tables also include the values of equilibrium constants obtained for hydroxo species.

From these tables the formation of ML species is well evidenced by significantly high values of log K^{M}_{ML}. However the major species in the investigated equilibria are hydroxo species which can be understood by the higher values of log $K^{ML}_{ML(OH)}$ and log $K^{ML(OH)}_{ML(OH)_2}$.

The values of equilibrium constants for various proton-ligand and metal-ligand systems were refined by applying the computer programme SCOGS [26]-[28]. These data were used to obtain the speciation curves. Analysis of these curves is discussed here under :

3.2 Organotin (IV)─Glycine / Alanine Systems (figures 3 and 6 and tables 2 and 3)

The nature of curves observed in the above refered figures suggest that in case of DMT (IV)-glycine / alanine system (figures 3 and 5) the concentration of free metal is quite low (20%) (curve 1) and the formation of ML species (curve 2) occurs from the initial pH and the reaches the maximum at pH≈4.0. The concentration of ML species is significantly high (≈90%). Above pH≈5.0 hydroxo complex exists as predominant species. In case of DOT (IV)-glycine / alanine system (figures 4 and 6) the concentration of free metal is high (approx.80%) as evidenced by curve 1 and the formation of ML species is evidenced at pH > 4.1 (curve 2).The percentage formation of ML species is about 50% which is low as compared to that observed in case of DMT (IV)-glycine system. This can be attributed to the steric crowding due to bulky nature of DOT (IV) cation . Above pH 4.5 the formation of hydroxo complex is evidenced as the major species (curves 3,4 in figures 5 and 6).

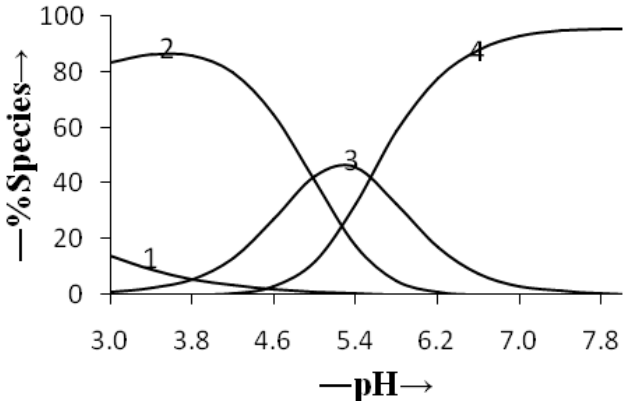

Figure 3: Speciation Curves for DMT (IV)-Glycine (1:1) System at 30±1°C[μ=0.10M($NaNO_3$)]

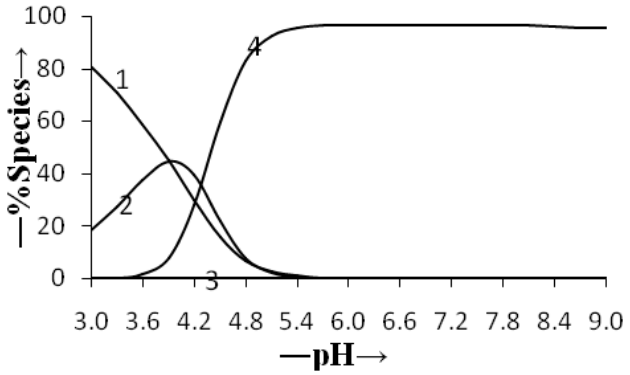

Figure 4: Speciation Curves for DOT(IV)-Glycine(1:1) System at 30±1ºC[μ=0.10M($NaNO_3$)]

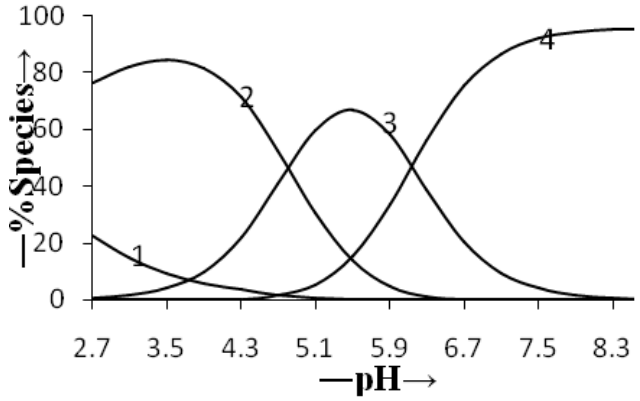

Figure 5: Speciation Curves for DMT (IV)-Alanine (1:1) System at 30±1ºC[μ=0.10M($NaNO_3$)]

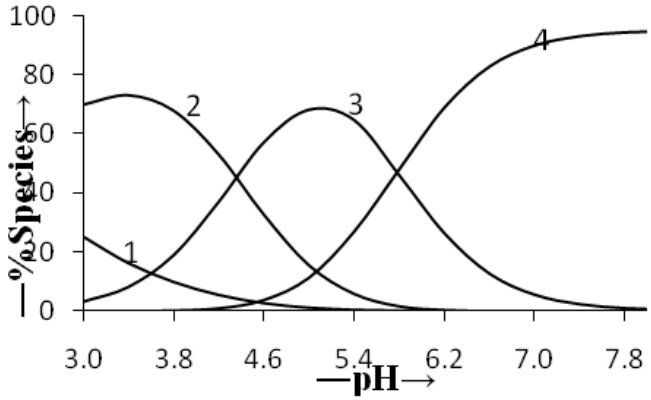

Figure 6: Speciation Curves for DOT(IV)-Alanine (1:1) System at 30±1ºC[μ=0.10M($NaNO_3$)]

Where,
Curve 1 : [M]; 2 : [ML]; 3 : [ML(OH)]; 4 : [$ML(OH)_2$]
The values of the thermodynamic stability constant $K_{\mu\to0}$, are used to determine the standard free energy change (ΔG°) for the complexation reaction from Van't Hoff isotherm :

$$\Delta G^\circ = -2.303RT \ln K_{\mu\to0} \quad \text{-------1.3}$$

The Gibb's Helmholtz equation is :

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{--------1.4}$$

From 1.3 and 1.4

$$\log K_{\mu\to0} = \frac{-\Delta H^\circ}{2.303\,R}\frac{1}{T} + \frac{\Delta S^\circ}{2.303\,R} \quad \ldots 1.5$$

4. Conclusion

The results observed in case of organotin (IV) cation with amino acids is perhaps due to the preferable binding of dialkyltin (IV) cation with nitrogen as compared to oxygen (17). However, this prediction needs further support by spectroscopic studies. Complex formation is more prefered with alanine as compared to glycine. This is in accordance with the earlier reported results (29).

On observing the values recorded in tables 2 and 3 it is observed that complex formation decrease with increasing ionic strength and increasing temperature.It is seen that ΔG° decrease with increase in temperature. Negative value of ΔH° and positive value of ΔS° supports the favourable conditions for complex formation and it indicates that the reaction is exothermic in nature.

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Table 1: Protonation Constant of Ligands at different Temperatures and Ionic Strengths

Parameters	20°C				30°C				40°C			
	0.05 M	0.10M	0.15M	μ→0	0.05 M	0.10M	0.15M	μ→0	0.05 M	0.10M	0.15M	μ→0
Glycine												
$\log \beta_{HL}$	9.01	8.87	8.80	9.40	8.77	8.74	8.60	9.08	8.56	8.40	8.30	9.00
Alanine												
$\log \beta_{HL}$	9.20	9.04	8.84	9.55	8.84	8.82	8.80	8.95	8.21	8.18	8.14	8.50

Table 2: Thermodynamic Parameters of M (IV)- Glycine Systems

DMT(IV)-Glycine System

Parameter	20°C		30°C		40°C		-ΔH° kJmol^{-1}	ΔS° JK^{-1}mol^{-1}
	log $K_{\mu\to0}$	-ΔG° kJmol^{-1}	log $K_{\mu\to0}$	-ΔG° kJmol^{-1}	log $K_{\mu\to0}$	-ΔG° kJmol^{-1}		
$logK^{M}_{ML}$	9.00	50.49	8.90	51.63	8.80	52.74	19.15	107.22
$logK^{ML}_{ML(OH)}$	12.20	68.44	11.80	68.46	11.81	70.78	37.34	105.34
$logK^{ML(OH)}_{ML(OH)2}$	14.20	79.66	14.15	82.09	14.10	84.50	9.57	239.33
DOT(IV)-Glycine System								
Parameter	**20°C**		**30°C**		**40°C**		**-ΔH° kJmol^{-1}**	**ΔS° JK^{-1}mol^{-1}**
	log $K_{\mu\to0}$	**-ΔG° kJmol^{-1}**	**log $K_{\mu\to0}$**	**-ΔG° kJmol^{-1}**	**log $K_{\mu\to0}$**	**-ΔG° kJmol^{-1}**		
$logK^{M}_{ML}$	9.55	53.58	9.50	55.12	9.52	57.05	2.87	172.87
$logK^{ML}_{ML(OH)}$	12.30	69.00	11.75	68.17	11.70	70.12	57.44	38.61
$logK^{ML(OH)}_{ML(OH)2}$	15.20	85.27	14.85	86.15	14.80	88.70	38.29	159.88

Table 3: Thermodynamic Parameters of M (IV)- Alanine Systems

DMT(IV)- Alanine System

Parameter	20°C		30°C		40°C		-ΔH° kJmol^{-1}	ΔS° JK^{-1}mol^{-1}
	log $K_{\mu\to0}$	-ΔG° kJmol^{-1}	log $K_{\mu\to0}$	-ΔG° kJmol^{-1}	log $K_{\mu\to0}$	-ΔG° kJmol^{-1}		
$logK^{M}_{ML}$	9.30	52.17	9.10	52.79	9.00	53.94	28.70	80.09
$logK^{ML}_{ML(OH)}$	12.00	67.32	11.75	68.17	11.70	70.12	28.72	131.50
$logK^{ML(OH)}_{ML(OH)2}$	14.70	82.47	14.35	83.25	14.34	85.94	34.46	163.20
DOT(IV)-Alanine System								
Parameter	**20°C**		**30°C**		**40°C**		**-ΔH° kJmol^{-1}**	**ΔS° JK^{-1}mol^{-1}**
	log $K_{\mu\to0}$	**-ΔG° kJmol^{-1}**	**log $K_{\mu\to0}$**	**-ΔG° kJmol^{-1}**	**log $K_{\mu\to0}$**	**-ΔG° kJmol^{-1}**		
$logK^{M}_{ML}$	10.00	56.10	9.65	56.08	9.60	57.53	38.29	60.31
$logK^{ML}_{ML(OH)}$	13.10	73.49	12.65	73.40	12.60	75.51	47.87	86.80
$logK^{ML(OH)}_{ML(OH)2}$	15.60	87.52	15.65	90.79	15.55	93.19	4.79	282.89

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